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Original paper

Distribution of phenols related to self-heating and water washing on coal-waste dumps and in coaly material from the Bierawka river (Poland)

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Abstract. Several types of coal waste (freshly-dumped waste, self-heated waste and waste eroded by rain water), river sediments and river water were sampled. The aim was to identify the types of phenols present on the dumps together with their relative abundances. Gas chromatography-mass spectrometry (GC-MS) analyses of a large number of samples (234) statistically underpin the phenol distributions in the sample sets. The largest average relative contents (1.17-13.3%) of phenols occur in the self-heated samples. In these, relatively high amounts of phenol, C1- and C2-phenols reflect the thermal destruction of vitrinite. In fresh coal waste, C2- and C3-phenols that originated from the bacterial/fungal degradation and oxidation of vitrinite particles are the most common (0.6 rel.%). Water-washed coal waste and water samples contain lower quantities of phenols. In the river sediments, the phenols present are the result of bacterial- or fungal decay of coaly organic matter or are of industrial origin.

Key-words: coal waste, GC-MS, phenols, water-washing, self-heating, fluvial transport

1. Introduction

Coal waste dumps are a typical element of the landscape in the Upper Silesian Coal Basin (USCB), Poland. Thus, the nature of the chemical compounds that can be leached from these dumps into their surroundings is a matter of some interest. Several processes such as biodegradation, water-washing and self-heating occur in these dumps. All are

processes that make potentially harmful compounds available for later transport out of the dumps.

The paper focuses on the distribution and general types of phenols related to their possible origin in selected coal-waste dumps and in coaly material in river sediments. Coal-waste dumps (or coal waste that has undergone self-heating) contain phenols related to the composition of vitrinite (Skręć et al. 2010; Misz-Kennan 2010; Misz-Kennan, Fabiańska 2010, 2011). As phenols easily dissolve in water, they are prone to leaching. Potential environmental hazards of phenols are related to their toxicity; they irritate skin and cause necrosis, damage kidneys, liver, muscle and eyes, and are carcinogenic (Clayton, Clayton 1994; EPA 2000; Michałowicz, Duda 2007). Phenols are widespread pollutants. They are introduced into natural water resources in the effluents of industrial chemical plants involved with, e.g., phenol manufacturing - coal tar, pharmaceuticals, resins, paints, dyes, textiles, wood, petrochemicals and pulp mills (Fleeger et al. 2003; Mukherjee et al. 1990). These common water pollutants associated with a wide variety of organic chemicals (Gad, Saad 2008). In soils, phenols can exist in a dissolved form that can move freely in the soil solution, in a sorbed form which reversibly binds to soil particles or proteins, and in a polymerized form consisting of humic substances (Hättenschwiler, Vitousek 2001; Freeman et al. 2001; Rovira, Vallejo 2002).

Some phenols are formed by natural processes, e.g., the formation of phenol and *p*-cresol during organic-matter decomposition or the synthesis of chlorinated phenols by fungi and plants (Swarts et al. 1998). Lignin-sourced macromolecules, a major component of vitrinite macerals, are widespread in sedimentary organic matter, particularly coals of kerogen III type. The major chemical structural elements in vitrinites are simple phenols with a high contribution of *para* alkyl-substituted derivatives (Killops, Killops 2005; Iglesias et al. 2000). Lignin is a macromolecular polyphenolic compound originating from the cell walls of vascular plants; it is formed by condensation reactions (involving dehydrogenation and dehydration) between three main building blocks, namely, coumaryl-, coniferyl- and sinapyl alcohols (Hedges, Ertel 1982; Killops, Killops 2005). Phenol and alkyl phenols are the most prominent products of the degradation of both lignin itself and lignin-derived macromolecules in coal (Saiz-Jimenez, De Leeuw 1985; Hatcher et al. 1992; Iglesias et al. 2002). Alkylphenols associated with short-chain (C_1 - C_3) methoxy-substituted alkylphenols, are typical pyrolysis products of unaltered- or weakly-altered lignin that reflect a terrigenous input (Martin et al. 1979; Obst 1983; Garcette-Lepecq et al. 2000; Faure et al. 2004). The series of methoxyphenols is formed from the thermal breakdown of lignin, and monosaccharide derivatives from cellulose. These derivatives of syringyl alcohol bound in lignin and include mainly syringic acid, syringyl acetone, acetosyringone and the dimer species disyringyl (Simoneit et al. 1993; Simoneit 2002; Ré-Poppi, Santiago-Silva 2002; Simoneit et al. 2007). In addition, angiosperm lignin contains high concentrations of the sinapyl- as well as coniferyl alcohol subunits which are the precursors to the syringol- and methoxyphenol degradation products from oxidation or pyrolysis (Hedges, Ertel 1982). The alkylphenols mainly arise from higher plants (Damsté, de Leeuw 1995). The formation of 2,4-dimethylphenol is believed to occur during the transformation of catechol-like structures into phenolic structures which takes place, in a selective manner, during coalification from lignite to subbituminous coal (Hatcher et al. 1988, 1989). Fabiańska and Kurkiewicz (2013) showed that in the pyrolysates of detrital lignites, phenol

and its *para* substituted derivatives such as *p*-cresol, *p*-vinylphenol, and *p*-ethylphenols predominate, indicating lignin structures of herbaceous plants (mostly monocotyledons) that are rich in coumaryl-alcohol units (Hatcher, Clifford 1997).

2. Study areas

In the USCB, the coals range from subbituminous- to high-volatile bituminous coals (Kotarba et al. 2002). The general features of the organic matter contained in the coal waste are similar to those of the bituminous coals (Fabiańska et al. 2013). Most of the organic matter was deposited in an estuarine/deltaic environment with normal- to low-water levels. The coals are early matured with similar vitrinite reflectance, and thermal maturity corresponding to early- and medium catagenesis (Fabiańska et al. 2013).

The study area, situated in the Rybnik Industrial Region, comprises four coal waste dumps and a river highly polluted by coal mining and processing (Fig. 1).

1. The coal-waste dumps in Szczygłowiec (ca 2.1 million tonnes of waste) and Trachy (ca 47.5 million tonnes) have been used since 1963. They are located along the Valley of Bierawka River. In the case of the Szczygłowiec dumps, there has been significant material transport into the Bierawka River from the steep slopes.
2. The Czerwionka-Leszczyny dump is forested and consists of three cones (~ 100 meters high). Intensive pseudo-fumarolic activity occurs on the top of the highest steep cone; gas vents on the surface are surrounded by sulphate crusts and puddles of bitumen (Parafiniuk, Kruszewski 2010). The thermal activity, which has continued for more than 30-40 years, is currently waning (Nádudvari 2014).
3. The Rymer dump is closed at present. The original waste material was essentially burnt out. From 1994-1999, the cones were redeveloped and spread out with additional coal-waste materials. However, as the original burnt-out material was hot, burning restarted in this added coal waste (Tabor 2002). Around the turn of the XXI Century, the surface of this dump was covered by concrete panels to block air access. Despite these, the self-heating intensified. Finally, the panels were removed from the western part. Today, heating occurs mostly on the eastern slope still covered by panels. Bitumen leaches out through cracks in these (Misz-Kennan et al. 2013).
4. The Bierawka River is a tributary of the upper part of the Odra River in southern Poland. Mine drainage has led to increasing sulphate-, sodium- and chloride concentrations in the water (Sracek et al. 2010). The period around 1800 was one of local industrial development based on local- and imported iron ores, charcoal production and hard coal exploitation (Klimek et al. 2013). The influence of coal mining and processing, and coking plants, is clearly evident in the river sediments; black layering is defined by mixtures of fine coal and sediment along the entire river course (Nádudvari, Fabiańska 2015). The river also passes by two coal-waste dumps (Szczygłowiec, Trachy; Fig. 1).

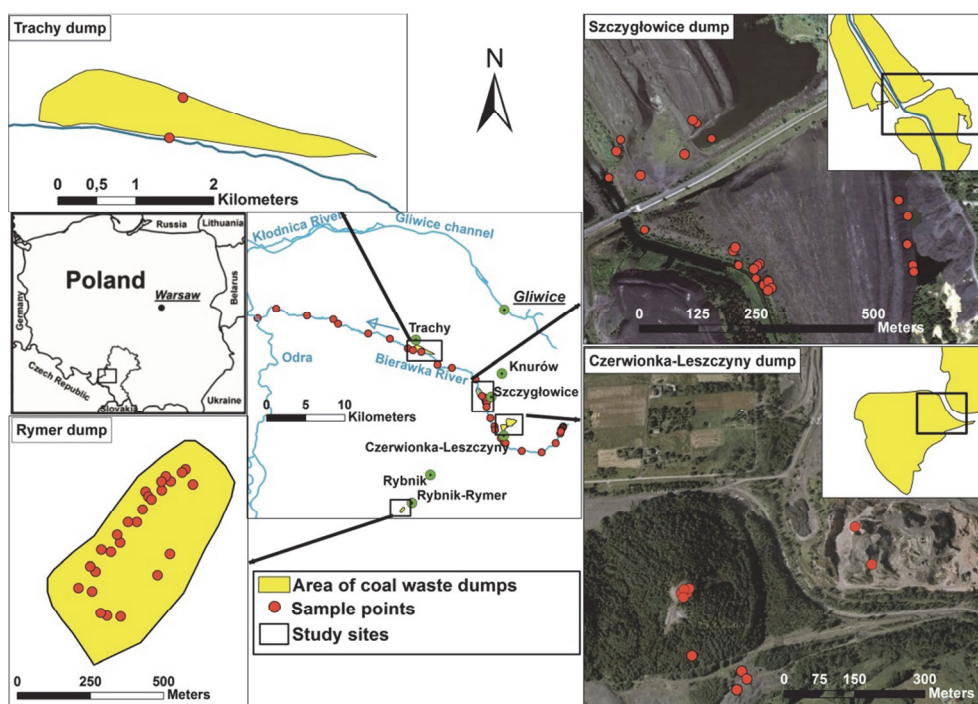


Fig. 1. The locations of the sites studied together with sampling points.

3. Methodology and materials

Samples of self-heated- and water-washed waste, fresh coal waste and river sediment from the bank of the Bierawka River were collected. For each sample, ca 1-2 kg material was taken at a depth of 5-10 cm. In total, 234 sample extracts were analyzed by gas chromatography-mass spectrometry (GC-MS). The sample set comprises: (a) Freshly-dumped (a few weeks before) coal waste taken from the Szczygłowiec dump (7 samples) and from the Trachy dump (2 samples). (b) Samples from erosion gullies taken from the Czerwionka-Leszczyny (4 samples) and Szczygłowiec dumps (36 samples). (c) 12 water samples from the Szczygłowiec dump collected, after heavy rains, from gullies that enter the Bierawka River. (d) Self-heated samples from the Czerwionka-Leszczyny dump (11 samples) and from the Rymer dump (85 samples) and (e) 47 sediments and 31 water samples collected from the entire course of the Bierawka River.

The samples of coal-waste and sediments were dried at room temperature (ca 22°C) for ca 5 days and powdered in a rotary mill to 0.2 mm grain size. Each sample was cleaned manually to remove surface contamination (roots, boughs, grass). After powdering, 15-20 g of each sample was extracted in dichloromethane (DCM) in a Dionex 350 apparatus dedicated to accelerated solvent extraction.

For water samples, ca 1 dm³ was taken at each sampling point. Several samples, mostly waters from erosion gullies on the Szczygłowiec dump had to be filtered once as they

contained a light fraction of sediment. Dissolved organic compounds were isolated using solid phase extraction (SPE) on 60 ml C₁₈ PolarPlus columns (BAKERBOND) with 500 mg of solid phase bonded on silica gel (40 µm APD, 20 Å). About 0.5 dm³ of water mixed with isopropanol (analytical) in the ratio 50 : 3 (vol.) was passed through the conditioned columns. Adsorbed organic compounds were eluted with a mixture of dichloromethane (DCM) and hexane.

The extracts were not separated into different compound groups prior to GC–MS analyses due to the very low extractability of some of the samples. All extracts (water, coal waste and sediments) were analyzed on an Agilent 7890A gas chromatograph with J&W HP-5MS, DB-5, DB-35 and DB-17MS columns coupled to a 5975C XL MDS mass spectrometer. Conditions were as follows: carrier gas, He; temperature programs: 50°C (2 min) to 175°C at 10°C/min, to 225°C at 6°C/min and to 300°C (held for 20 min) at 4°C/min. The spectrometer was operated in the electron ionisation (EI) mode (70 eV, full scan) and scanned from m/z 50-650. Compounds were identified by using their mass spectra, comparison of peak retention times with those of standard compounds, interpretation of MS fragmentation patterns and literature data (Philp 1985; The Wiley/NBS Registry of Mass Spectral Data 2000). Phenols were manually integrated (peak areas) using their mass spectra (94, 108, 122, 136, 150 m/z). The results were semi-quantitatively analysed to assess the relative percentage of phenols in each sample. Thus, each peak areas of the chromatogram (together with phenols) had to be manually integrated. Then, each peak areas were compared to the total peak area of the whole chromatogram (calculated in percentages). Later, the assessed phenol percentages were summarised to see how much of the entire chromatogram contained only phenols.

4. Results and discussion

The samples contain a wide range of phenols represented by phenol, C₁-phenols (methylphenols); C₂-phenols (dimethylphenol, and ethylphenols) and lower relative percentages of C₃-phenols (trimethylphenols, methyl-ethylphenols, propylphenols) and C₄-phenols (*tert*-butylphenols, dimethylethylphenols, methylpropylphenols, 4-vinyl-methoxylphenols) as shown on Figure 2. The exact distribution of phenols can be influenced by many factors, e.g., organic-matter origin and its rank (Hatcher et al. 1992; Skrzęta et al. 2010).

4.1. Phenols released by organic-matter oxidation and water washing

Generally, the fresh coal wastes contain 0.66 rel.% of phenols, mostly dimethylphenols (C₂-phenols) and, e.g., 3-ethyl-5-methylphenol (C₃-phenols) as shown in Table 1. The presence of phenols in fresh coal waste can be explained by the findings of Swann and Evans (1979) on brown coal oxidation; oxygen gained in the solid phase during oxidation accounts for increased amounts of carboxyl-, carbonyl- and phenolic groups. Short storage times eliminated the possibility of any leaching by water. In addition, bacterial and fungal degradation of vitrinite particles in coal waste can also release phenols (Orem et al. 2010; Haider et al. 2013).

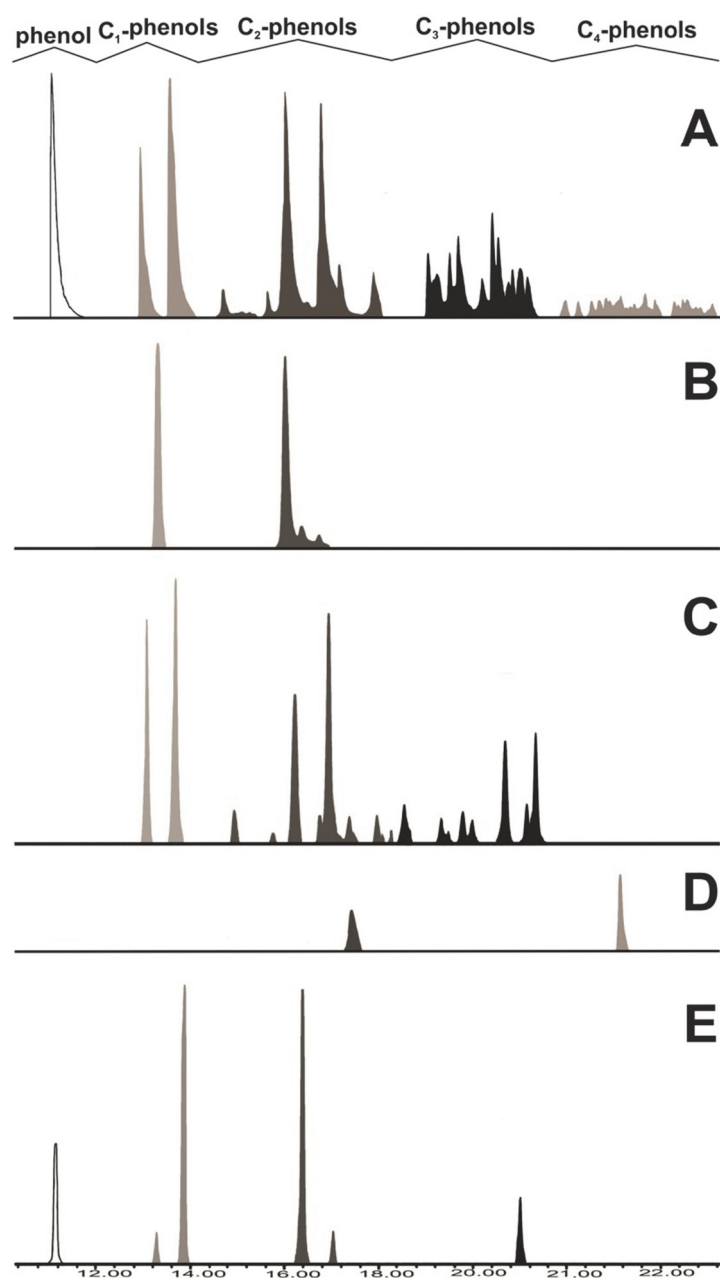


Fig. 2. Representative chromatograms for phenols from the different sample groups. A: Fresh coal wastes. B: Samples from erosion gullies from Szczygłowice- and Czerwionka-Leszczyny dumps. C: Czerwionka-Leszczyny self heated samples. D: Water samples from Bierawka River. E: River sediments from Bierawka River. (Phenol: m/z 94. C_1 -phenols: m/z 108. C_2 -phenols: m/z 122. C_3 -phenols: m/z 136. C_4 -phenols: m/z 150)

Table 1. The distribution of relative percentage contents and most common phenol compounds in the analysed sample groups. Identification of phenols was made by comparison of their mass spectra and peak retention times with those of standard compounds, and using literature data. The relative average % contents represent the summarised phenols of each chromatogram in each sample group.

Analysed sample groups	The most common phenols	Relative average % contents	Number of samples which contained phenols	Number of samples, where phenols were absent
Fresh coal wastes (Szczygłowiec -and Trachy dumps)	2,3-dimethylphenol (m/z 122); 2,4-dimethylphenol (m/z 122); 2,6-dimethylphenol (m/z 122); 3-ethyl-5-methylphenol (m/z 136)	0.66	8	0
Samples from erosion gullies (Szczygłowiec - and Czerwionka-Leszczyny dumps)	3-methylphenol (m/z 108); 4-methylphenol (m/z 108); 2,4-dimethylphenol (m/z 122)	0.35	4	36
Water samples from gullies of coal waste (Szczygłowiec dump)	4-methylphenol (m/z 108)	0.02	1	11
Self-heated samples from Czerwionka-Leszczyny dump	2-methylphenol (m/z 108); 4-methylphenol (m/z 108); 2,3-dimethylphenol (m/z 122); 2,4- dimethylphenol (m/z 122); 2,6- dimethylphenol (m/z 122); 2,5-dimethylphenol (m/z 122)	1.17	8	3
Self-heated samples from Rymer dump	phenol (m/z 94); 2-methylphenol (m/z 108); 3-methylphenol (m/z 108); 4-methylphenol (m/z 108); 2-ethylphenol (m/z 108); 3-ethylphenol (m/z 108); 2,3-dimethylphenol (m/z 122); 2,4-dimethylphenol (m/z 122); 2,5-dimethylphenol (m/z 122); 2,6- dimethylphenol (m/z 122); 3,4-dimethylphenol (m/z 122); 3,5-dimethylphenol (m/z 122); 2-ethyl-6-methylphenol (m/z 136); 3-ethyl-5-methylphenol (m/z 136); 2,3,5-trimethylphenol (m/z 136); 2,4,6-trimethylphenol (m/z 136); 2-methoxy-4-vinylphenol (m/z 150); phenol, 4-(1-methylpropyl) (m/z 150)	13.3	71	14
River sediments from the Bierawka River	phenol (m/z 94); 2-methylphenol (m/z 108); 4-methylphenol (m/z 108); 2,4- dimethylphenol; (m/z 122)	0.23	34	13
River water samples from the Bierawka River	2-dimethylphenol (m/z 122); 3- (1,1-dimethylethyl)phenol (m/z 150); 4-(1,1-dimethylethyl)phenol (m/z 150)	0.07	19	12

Of 40 gully samples from Szczygłowie and Czerwionka-Leszczyny, only four contain some phenols (Table 1), e.g., 3-methylphenol, 4-methylphenol, and 2,4-dimethylphenol (on average 0.35 rel.%). Furthermore, of twelve water samples taken after heavy rain from gullies on the Szczygłowie dump, only one contains phenols (4-methylphenol; 0.02 rel.%), because of the intensive water washing. As phenols are very soluble in water, they are easily leached and potentially washed into dump interiors or surroundings (Faksness, Brandvik 2008; Misz-Kennan 2010; Misz-Kennan, Fabiańska 2011, 2010; Skręt et al. 2010). In addition, in the Bierawka River sediments, the average relative percentage of phenols is elevated in the interval between the Szczygłowie dump and the Odra River (0.34%) as compared to the interval between the dump and the river source (0.11%); leaching from the Szczygłowie dump is indicated. Around the dump, several soil-water lakes reflect subsidence due to underground mining (Pelka-Gosciniak et al. 2008; Wojciechowski 2006). Associated with the mining activities, the river channel has become wider with the water level reaching the base of the dumps. Thus, the leaching of phenols is now even more likely.

4.2. The presence of phenols in sediment and river waters

Thirty-four sediment samples from the river contained phenols such as C₁- and C₂-phenols (on average, 0.23 rel. %; Table 1). The phenols in the river sediments show a similar pattern to those in the coal waste (Fig. 3); the presence of coal and coke particles is the reason.

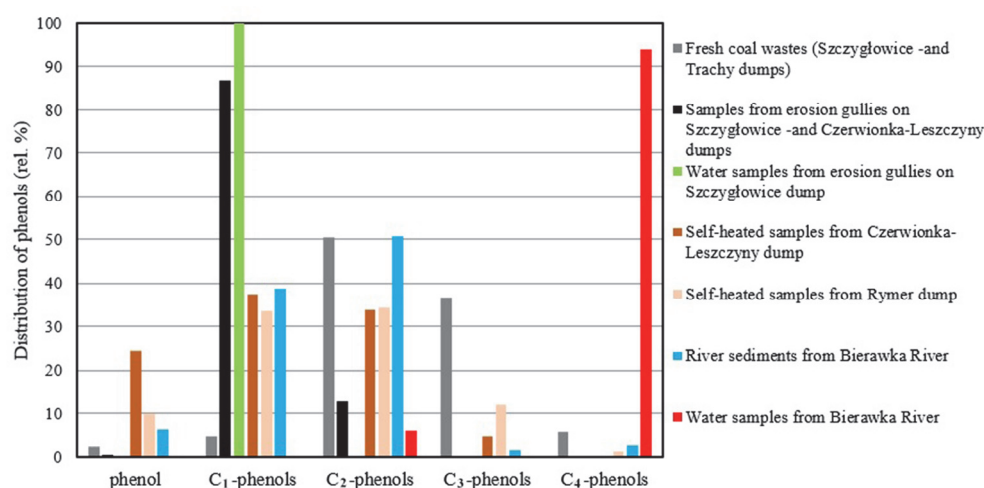


Fig. 3. Summarised relative percentages in the different sample groups compared to the total amount of phenol compounds.

The primary origin of the sediment-hosted coaly material is related not only to the coal processing but also to the dumping of a thousand tons of ash with unburned coal particles from an old glass factory near the river source. This material has been redeposited along the

entire river course. Hard-coal processing features (crushing–washing) are evident in larger coal fragments. Intensive erosion of the steep slopes of the Szczygłowiec coal-waste dump also transferred significant amounts of organic matter into the river (Nádudvari, Fabiańska 2015).

Phenols in river sediments may originate from factories, coke production or from the fungal- and/or bacterial degradation of the coaly sediments and other organic matter such as pine needles, leaves, grass and wood (Saiz-Jimenez, De Leeuw 1985; Faure et al. 1999; Orem et al. 2010; Haider et al. 2013). Methylphenols occur in high concentrations (up to several grams per kilogram) in coal tar. The representatives of methylphenols are cresols that form three isomers – ortho, meta and para-cresol. In addition, *o*-cresols, dimethylphenol and 2,4,6- trimethylphenol are also formed during coal- and gasoline combustion (Ioppolo-Armanios et al. 1995; McBrain et al. 1996). This may explain the presence of C₁ and C₂-phenols in the ash-bearing Bierawka sediments.

Nineteen river-water samples contained phenols (on average, 0.07 rel. %). The most common are C₄-phenols (Table 1, Fig. 3). Their origin is probably industrial or domestic. Moreover, phenols such as 3-(1,1-dimethylethyl)-4-methoxyphenol are used in cosmetics, rubber, pesticides, fungicides and bactericides (SAC 2010).

4.3. Phenol released from self-heated coal wastes

The extracts of the self-heated coal-waste samples contain the highest percentages of phenols; those from Czerwionka-Leszczyny 1.17% (on average) and those from Rymer 13.3%, the highest of all. Phenol, C₁-phenol, and C₂-phenols are the most abundant compounds, but heavier C₃- and C₄-phenols are present in smaller quantities (Fig. 3). As these compounds are released from vitrinite as a result of its thermal destruction, they may represent the relatively early stages of self-heating (Skręć et al. 2010). On the Rymer dump, as the current self-heating only started after the remediation of 15-20 years ago, phenols are present in especially significant amounts. Here, leaching and evaporation may have been limited by the covering of concrete panels (Nádudvari, Fabiańska 2016). In contrast, heating has continued for more than 30-40 years on the Czerwionka-Leszczyny dump. In this case, phenols are likely to have been destroyed by combustion, leached, and/or have evaporated.

High contents of phenols reflect the intensity of the thermal changes due to heating (Misz-Kennan, Fabiańska 2011). In addition, abundant phenols (with domination of C₁ - C₂ types) typify expelled bitumen mixed in with the waste. Furthermore, highly thermally-affected waste (mostly burned-out material) containing the lowest amounts of phenols (with domination of C₂ type) reflect the total destruction of vitrinites, and the ease of phenol leaching and evaporation (Nádudvari, Fabiańska 2016).

5. Conclusions

1. Fresh coal waste can be a source of phenols originating from bacterial/fungal degradation, and the oxygenation of vitrinite particles. These highly toxic pollutants should be prevented from migrating out into dump surroundings.

2. On the coal-waste dumps, gully- and water samples contain lesser quantities of phenols due to intensive water-washing. Leaching from the Szczygłowiec dump contributes to elevated phenol contents in the Bierawka River downstream from the dump.
3. The presence of identified phenols, notably C₁- C₂ phenols, in the sediments of the Bierawka River draws attention to what is likely a widespread phenomenon associated with coal processing. For example, similar environmental issues may characterize rivers in other coal mining districts in the region, e.g., the Kłodnica and Ruda Rivers. Phenols in river sediments may also reflect bacterial- or fungal decay of coaly matter in the sediments.
4. The fact that the highest contents of phenols (phenol, C₁- and C₂) derive from the thermal destruction of vitrinite is especially significant where self-heating is present on a coal-waste. Phenols as highly-toxic pollutants released from coal waste and by the coal processing industry should be given serious attention, especially in the environs of dumps sited close to urban areas.

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